



Structural and Surface Morphological Change in Incorporation of Magnesium on Synthesised Nano Hydroxyapatite

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Abstract

The complex apatite, Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) (HAp) has the hydroxyl group as end member with the Ca/P ratio 1.67. Nano Hydroxyapatite is mainly used in the bone tissue engineering and dental applications. Magnesium is one of the predominant substitutes for calcium in biological apatites. Mg substituted nano Hydroxyapatite are expected to have excellent biocompatibility and properties that can be favourably compared with those of hard tissue, and it stimulates osteoblast proliferation. The aim of this study is to synthesis and characterize the pure nano Hydroxyapatite and Mg doped nano Hydroxyapatite by sol-gel method. The functional group of the prepared samples were analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The nature and particle size of the prepared samples were analyzed by X-ray diffraction method (XRD). The surface morphology was analyzed using scanning electron microscope (SEM).

1. INTRODUCTION

Hydroxyapatite is a type of calcium phosphate similar to human hard tissue in morphology and composition (Wei and Ma, 2004). Hydroxyapatite is called as Bone mineral, because 70% weight of human bone is a form of hydroxyapatite (Kalita *et al.* 2007). Hydroxyapatite is coated for hip replacement, dental implants and bone conduction implants. Porous nature of hydroxyapatite is used for drug delivery. Comparing with other calcium phosphates, hydroxyapatite has more stability under temperature and pH. Hydroxyapatite has biocompatibility, bioactivity, osteoconductivity, non toxicity and non inflammatory nature. Nano hydroxyapatite is used for drug and gene delivery, bone tissue engineering, bone void fillers, desensitizing agent in post teeth bleaching and also a main component of enamel (Kantharia *et al.* 2014).

Calcium deficient hydroxyapatite, $\text{Ca}_{10-x}(\text{PO}_4)_6-x(\text{HPO}_4)_x(\text{OH})_{2-x}$ (where x is between 0 and 1) has a Ca/P ratio between 1.67 and 1.5 metals like Zn, Mn, Si, Mg, Ti, Cu, Co, etc., can be doped with calcium deficient hydroxyapatite in small amounts (Raynaud *et al.* 2002). This does not change the crystallographic properties intensely, and affect the mechanical and biological properties. Magnesium (Mg) is known to be an important trace element, particularly during the early stages of osteogenesis where it stimulates osteoblast proliferation and its depletion causes bone fragility and

bone loss. Furthermore, relationship has been suggested between the Mg content in enamel and the development of dental carries. Giving the biological relevance of Mg, many researchers have worked on the preparation of HAp and calcium phosphate implant materials containing low level of Mg, which has been showed to improve biological role of Mg. The presence of Mg in HAp inhibits crystallization, reduces crystal size and decreases the proliferation and activity of osteoblast like cells, while its deficiency affects all stages of skeletal metabolism, causing cessation of bone growth, decrease of osteoblastic and osteoclastic activities and bone fragility. In short, it is considered as one of the most important trace element in Hap (Daniella Laurencin *et al.* 2011).

2. MATERIALS & METHODS

0.8M of calcium nitrate tetra hydrate and 0.48M of diammonium hydrogen phosphate was stirred for ½ an hour with pH of the solutions were maintained separately at 10 using ammonium hydroxide solution. Then the phosphate solution is added drop wise to the calcium solution with vigorous stirring for 1 hour. Then the resultant solution was aged for 24 hours at room temperature. The impurities present in gel was removed by repeated washing with double distilled water and filtered using whatsmann No.1 filter paper. Then the filtered HAp gel is dried at 100 °C for 10 hours. The dried powder was grained with agate mortar and pestle

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into fine powder and subjected to calcinations at 300 °C temperature for 2 hrs using electrically heated furnace. For Mg-HAp 0.1M of magnesium nitrate hexahydrate was stirred separately for 10 minutes and added to the calcium containing solution and the same procedure is followed.

3. RESULT & DISCUSSION

3.1 FTIR Analysis

Infrared spectrometer determines the position and relative sizes of all the absorption peaks in the infrared region. Fig1: shows that vibrational modes of PO_4^{3-} and OH group characteristics of HAP. The peak around 3448.27 represent OH vibration of water. The peak around 1643.85 and 1381.04 is assigned to bending mode of water. The peak around 1034.82 and 566.11 represents the PO_4^{3-} vibrational mode.

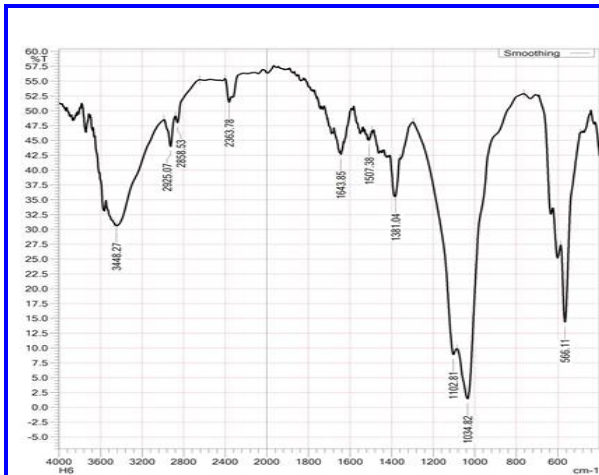


Fig. 1: FTIR spectrum of pure HAp

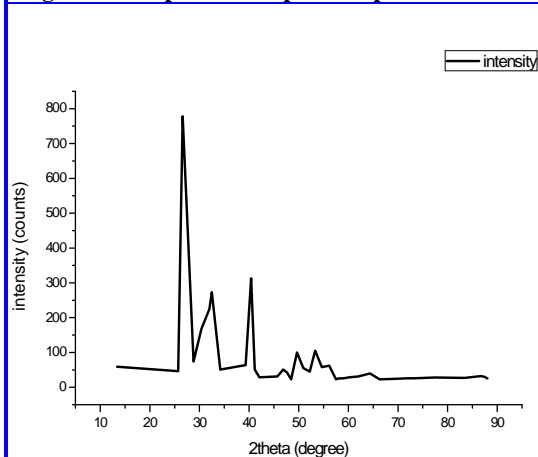


Fig. 3: XRD of pure HAp

Fig2: shows the Mg doped HAp, the peak around 3446.82 represents OH stretching vibration of water. The peak around 1639.02 and 1380.56 is assigned to bending mode of water. The peak around 1028.07 and 554.06 represents the PO_4^{3-} vibrational mode (Gozalian *et al.* 2011). Mg ions reduced the resolution of PO_4^{3-} band. And the intensity of the peak decreases by doping with Mg.

3.2 XRD Analysis

XRD analysis was used to examine the structural analysis of the prepared samples. Fig3. and Fig4. shows the XRD spectrum of pure and Mg doped nano HAp powders. The XRD pattern indicates the presence of sharp peaks (Kalita and Bhatt, 2007). The crystallite size, microstrain, Dislocation density of the synthesized powders can be calculated and listed in table1 and table 2.

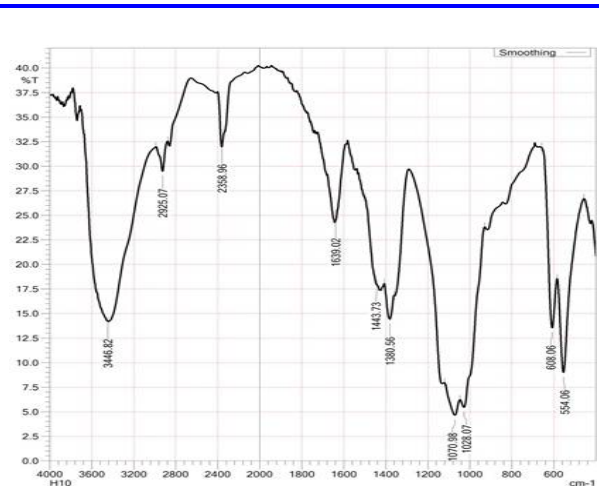


Fig. 2: FTIR spectrum of Mg-HAp

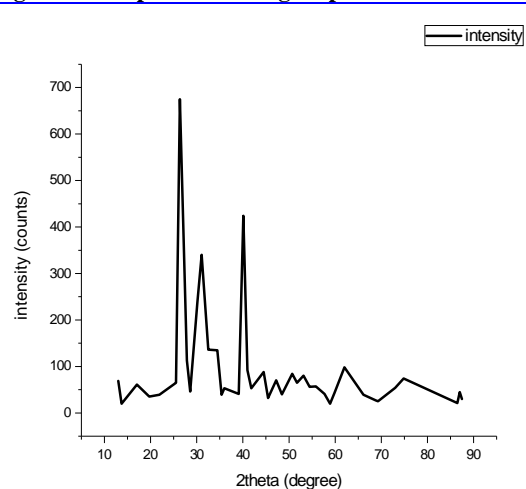


Fig. 4: XRD of Mg- HAp

Table 1. Pure Hydroxyapatite

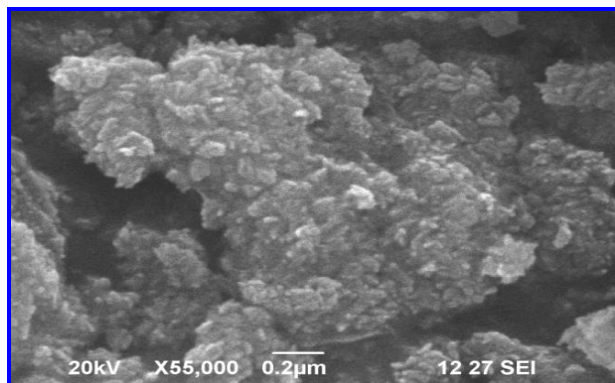
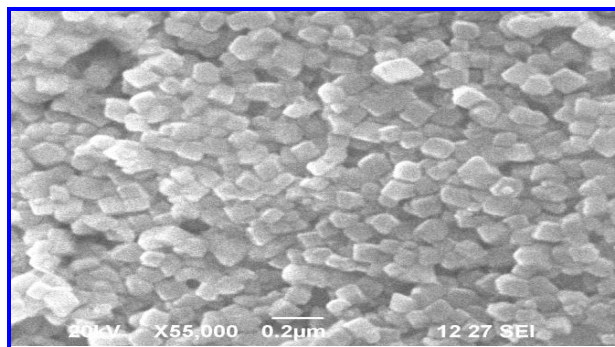
| 2θ (deg) | d (\AA) | FWHM (deg) | Crystallite size (nm) | Microstrain 10^{-3} m | Dislocation density 10^{15} lines/m |
|-----------------|----------------------|------------|-----------------------|-------------------------|---------------------------------------|
| 26.6294 | 3.34478 | 0.53030 | 15.39 | 2.2518 | 4.2228 |
| 40.3139 | 2.23539 | 0.53520 | 15.81 | 2.1922 | 4.0007 |
| 32.5000 | 2.75275 | 1.50200 | 5.36 | 6.2594 | 34.807 |

Table 2. Mg- Hydroxyapatite

| 2θ (deg) | d (\AA) | FWHM (deg) | Crystallite size (nm) | Microstrain 10^{-3} m | Dislocation density 10^{15} lines/m |
|-----------------|----------------------|------------|-----------------------|-------------------------|---------------------------------------|
| 26.3384 | 3.38107 | 0.51350 | 15.88 | 2.1816 | 3.9640 |
| 40.1069 | 2.24645 | 0.49380 | 17.12 | 2.0240 | 3.4119 |
| 31.0619 | 2.87684 | 0.52950 | 15.57 | 2.2260 | 4.1272 |

3.3 SEM Analysis

SEM images of the prepared samples are shown in fig. 5 and fig 6. For pure nano hydroxyapatite the surface morphology appears irregular in shape and agglomerated. But for Mg-HAp the surface morphology improved with cubic shape (Arghavan Farzadi *et al.* 2014). This in turn reveals the surface modification and improvement in the surface morphology takes place due to incorporation of Magnesium.

**Fig. 5: SEM image of pure HAp****Fig. 6: SEM image of Mg-HAp**

4. CONCLUSION

The nano size pure HAp and Mg doped HAp was prepared by sol-gel technique. The synthesized nano powders were studied for their functional group, crystallite size and surface morphology. The presence of functional group and their vibration mode in pure HAp and Mg-HAp were analysed using the FTIR spectrum. The intensity of peaks decreases by doping with Magnesium. The crystalline nature and crystallite size of the HAp nano powders were analysed from the peaks. Average crystallite size was calculated using scherrer's formula. For pure and Mg doped HAp the crystallite size were 12.187 nm & 16.19 nm respectively. It was found that the crystallite size of HAp increased by addition of the dopant. The SEM provides the detailed information about the surface morphology of pure and Mg doped HAp at the microscopic level.

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